PB82-156050

The Determination of Dithiocarbamate Pesticides in Industrial and Municipal Wastewaters: Method 630

(U.S.) Environmental Monitoring and Support Lab.-Cincinnati, OH

Feb 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-156050

THE DETERMINATION OF DITHIOCARBAMATE PESTICIDES IN INDUSTRIAL AND MUNICIPAL WASTEWATER

Method 630

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January 1982

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U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-011	REPORT	PB82 156050

4. TITLE AND SUBTITLE	5. REPORT DATE
The Determination of Dithiocarbamate Pesticides in Industrial and Municipal Wastewaters Method 630	Feb. 1982
	6. PERFORMING ORGANIZATION CODE 033009
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas A. Pressley and James E. Longbottom	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Monitoring and Support Lab - Cincinnati Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268	ABEB1C
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Same as Above	Final
	14. SPONSORING AGENCY CODE EPA/600/6

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This is a colorimetric method applicable to the determination of selected pesticides in municipal and industrial discharges as provided under 40CFR 136.1. A sample is digested with acid to yield carbon disulfide by hydrolysis of dithiocarbamates. The evolved CS_2 is trapped in a color reagent and absorbance is measured at 380 and 435 nm.

The compounds included in the method scope are: amobam, Busan 40, Busan 85, ferbam, KN methyl, mancozeb, maneb, metham, nabam, niacide, polyram, sodium dimethyldithiocarbamate, thiram, zineb, and ziram.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	15
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

THE DETERMINATION OF DITHIOCARBAMATE PESTICIDES IN INDUSTRIAL AND MUNICIPAL WASTEWATER

METHOD 630

1. Scope and Application

1.1 This method covers the determination of dithiocarbamate pesticides. The following parameters can be determined by this method:

Parameter	STORET No.	CAS. No.
Amobam	--	3566-10-7
AOP	--	--
Busan 40	--	--
Busan 85	--	--
Ferbam	--	14484-64-1
KN Methyl	--	--
Mancozeb	--	8065-67-6
Maneb	--	12327-38-2
Metham	--	137-42-8
Nabam	--	142-59-6
Niacide	--	8011-66-3
Polyram	--	9006-42-2
Sodium dimethyldithiocarbamate	--	128-04-1
Thiram	--	137-26-8
ZAC	--	--
Zineb	--	12122-67-7
Ziram	--	137-30-4

1.2 This method fails to distinguish between the individual dithiocarbamates. The compounds above are reduced to carbon disulfide and the total dithiocarbamate concentration is measured. Unless the sample can be otherwise characterized, all results are reported as Ziram. Carbon disulfide is a known interferent.

1.3 This is a colorimetric method applicable to the determination of the compounds listed above in industrial and municipal discharges as provided under 40 CFR 136.1. Any modification of this method beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.4 The method detection limit (MDL, defined in Section 12) for maneb, metham and ziram are listed in Table 1. The MDL for a specific dithiocarbamate or wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 This method is restricted to use by or under the supervision of analysts experienced in trace organic analyses. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1 liter, is digested with acid to yield carbon disulfide by hydrolysis of the dithiocarbamate moiety. The evolved CS_2 is purged from the sample and absorbed by a color reagent. The absorbance of the solution is measured at 380 and 435 nm using a UV-visible spectrophotometer.[1]

3. Interferences

3.1 Method interferences may be caused by contaminants in reagents, glassware and other sample processing hardware that lead to high blank values and biased results. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.[2] After each use, rinse the decomposition flask and condenser with 4N NaOH and reagent water. Overnight soaking in 4N NaOH may be necessary. Clean the H_2S scrubber between each use with 0.1N HCl in methanol, rinse three times with methanol and bake at 200°C for 15 min. Rinse the CS_2 trap with methanol three times between each use and follow by heating for 15 min at 200°C. Should it become difficult to force the color reagent through the glass frit of the CS_2 trap, clean in the same manner as the H_2S scrubber. After cooling, store glassware sealed to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems.

3.2 Carbon disulfide may be a significant direct interferent in wastewaters. Its elimination or control is not addressed in this method. If correction for background carbon disulfide is required, the CS_2 should be measured by an independent procedure, such as direct aqueous injection gas chromatography.

3.3 Additional matrix interferences may be caused by contaminants that are codistilled from the sample. The extent of matrix interfer-

ences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup provided by the H_2S trap will eliminate or reduce some of these interferences, but unique samples may require additional clean-up approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle - Amber borosilicate or flint glass, 1-liter or 1-quart volume, fitted with screw caps lined with TFE-fluorocarbon. Aluminum foil may be substituted for TFE if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing must be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Dithiocarbamate hydrolysis apparatus (Figure 1) - (Available from Southern Scientific Inc., Box 83, Micanopy, Florida 32267). Apparatus includes the following or equivalent components:

5.2.1 Hot plate with magnetic stirrer.

5.2.2 Hydrolysis flask - 2 L, flat bottom with ground glass joints, 2 necks.

5.2.3 Condenser - low internal volume, ground glass joints, Liebig (Kontes K-447000, 100 mm or equivalent).

5.2.4 Gas washing bottles - 125 mL, with extra-coarse porosity (Kontes K-657750 or equivalent).

5.2.5 Addition funnel - 60 mL, ground glass joint to fit hydrolysis flask, with long stem to reach at least 2 cm below the liquid level in the hydrolysis flask.

5.2.6 Dust trap (Adapter) - to fit top of addition funnel (Kontes K-174000 or equivalent).

5.2.7 Vacuum source - stable pressure with needle valve for control.

5.3 UV-Visible spectrophotometer - Double beam with extended cell path length capability of 1.0 and 4.0 cm cells.

5.4 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 gram. The preparation of calibration standards for some dithiocarbamates (e.g. metham) requires the use of a balance capable of weighing 10 µg.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest. Prepare by boiling distilled water 15 min immediately before use.

6.2 Acetonitrile, diethanolamine, methanol - ACS grade.

6.3 Ethanol - 95%.

6.4 Cupric acetate - Monohydrate, ACS grade.

6.5 Hydrochloric acid - Concentrated.

6.6 Hydrochloric acid, 0.1 N in methanol - Slowly add 8.3 mL conc. HCl to methanol and dilute to 100 mL.

6.7 Sodium hydroxide, 4 N - Dissolve 16 g ACS grade NaOH pellets in reagent water and dilute to 100 mL.

6.8 Stannous chloride - $SnCl_2 \cdot 2H_2O$, ACS grade.

6.9 Zinc acetate solution, 20% - Dissolve 20 g ACS grade $Zn(C_2H_3O_2) \cdot 2H_2O$ in reagent water and dilute to 100 mL.

6.10 Color reagent - Add 0.012 g cupric acetate monohydrate to 25 g diethanolamine. Mix thoroughly while diluting to 250 mL with ethanol. Store in amber bottle with TFE-fluorocarbon-lined cap.

6.11 Decomposition reagent - Dissolve 9.5 g stannous chloride in 300 mL conc. hydrochloric acid. Prepare fresh daily.

6.12 Stock standard solutions (1.00 µg/µL) - Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions.

6.12.1 Prepare a stock standard solution for ziram by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in acetonitrile and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.12.2 Transfer the stock standard solution into a TFE-fluorocarbon-sealed screw cap vial. Store at 4°C and protect from light. Frequently check stock standard solutions for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.12.3 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.

6.12.4 When using other dithiocarbamates for calibration, such as maneb or metham, it may be necessary to weigh microgram amounts of the pure material into small aluminum foil boats and place them directly in the hydrolysis flask.

7. Calibration

7.1 Use ziram as the standard for total dithiocarbamates when a mixture of dithiocarbamates is likely to be present. Use the specific dithiocarbamate as a standard when only one pesticide is present and its identity has been established.

7.2 With the apparatus assembled and reagents in place, Section 10, pour 1500 mL of reagent water into each decomposition flask, add 30 mL of decomposition reagent and start aspiration.

7.3 Spike the water in each flask with an accurately known weight of dithiocarbamate standard. Use a series of weights equivalent to 5-200 µg of CS_2. Follow the procedure outlined Section 10.

7.4 Prepare calibration curves at a minimum of three concentrations by plotting absorbance vs. weight of dithiocarbamate. A separate curve is prepared from readings taken at 435 nm and at 380 nm for each cell path length used. Normally the 435 nm curve is used for calibration above 30 µg ziram (4 cm cell), and the 380 nm curve is used for calibration below 30 µg ziram. The choice of which curve to use is left to the discretion of the analyst. It is recommended that the curves be transformed into mathematical equations using linear least squares fit for the data from 435 nm and quadratic least squares fit for data from the 380 nm.

7.5 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

8. Quality Control

8.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured.

8.2.2 Add the known amount of dithiocarbamate standard to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results.

Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 1, determine the recovery and single operator precision expected for the method, and compare these results to the values calculated in Section 8.2.3. If the data are not comparable, review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance as follows:

$$\text{Upper Control Limit (UCL)} = R + 3s$$
$$\text{Lower Control Limit (LCL)} = R - 3s$$

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternatively, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.4 The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one spiked sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 11.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a 1-liter aliquot of reagent water that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of quality control materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of plastic and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

9.3 All samples must be analyzed within seven days of collection.

10. Sample Analysis

10.1 Assemble the hydrolysis apparatus as follows (See Figure 1):

10.1.1 Place the hydrolysis flask on the hot plate.

10.1.2 Place the addition funnel in one of the necks of the hydrolysis flask and the dust trap in the top of the funnel.

10.1.3 Place the condenser in the other neck and attach two gas washing bottles in succession to the condenser outlet.

10.1.4 Attach a vacuum line with a flow valve to the second scrubber .

10.2 Allow the sample to warm to room temperature. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the 2-liter hydrolysis flask. Rinse the bottle four times with 100-mL aliquots of reagent water, adding the washes to the hydrolysis flask. Bring the volume in the hydrolysis flask to approximately 1,500 mL with reagent water.

10.3 Place 15.0 mL of color reagent into the CS_2 trap (second gas washing bottle). Place 9 mL of zinc acetate solution into the H_2S scrubber (first gas washing bottle). Add 2 mL of ethanol to the H_2S scrubber. Place a magnetic stirring bar in the hydrolysis flask and place the flask on the hot plate/magnetic

stirrer (ambient at this time). Assemble the apparatus providing adequate support for all glassware. The addition funnel stem opening must be below the water level. Ground glass joints may be slightly coated with silicone grease.

10.4 Start the stirrer, begin water flow through the condenser, and turn on hot plate and begin heating the flask. Open the needle valve slightly and start the aspirator. By closing the needle valve, adjust the airflow through the absorption train until the proper flow is attained. (The column of bubbles extends to the bottom of the spherical expansion chamber at the top of the CS_2 trap.) Add 30 mL of decomposition reagent to the flask. (Note: The analyst must ensure that the sample pH is less than 2 during hydrolysis.)

10.5 Bring the liquid in the flask to a gentle boil. Continue the boiling for 60 minutes, then remove the heat. Continue aspiration until boiling ceases.

10.6 Transfer the contents of the CS_2 trap into a 25.0 mL volumetric flask by forcing the liquid through the glass frit and out of the inlet arm with pressure from a large pipet bulb. Ensure quantitative transfer by rinsing the trap three times with ethanol. Bring the colored solution to volume with ethanol. Mix thoroughly and allow the color to develop for at least 15 min but not more than two h before determining the absorbance.

10.7 Determine the absorbance of the sample at 435 nm and 380 nm using a 1-cm cell or a 4-cm cell as necessary. Determine the weight of dithiocarbamate from the appropriate calibration curve prepared in 7.4.

10.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. If a smaller measured aliquot of sample was used to remain within the range of the color reagent, this step may be omitted.

11. Calculations

11.1 Determine the concentration of total dithiocarbamates in the sample as ziram directly from the calibration curve. When a specific dithiocarbamate is being measured, quantitate in terms of the selected pesticide.

11.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

11.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in 8.3, data for the affected parameters must be labeled as suspect.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[8] the MDL concentrations listed in Table 1 were determined using wastewater, and are expressed in concentration units of the spiked materials.[1]

12.2 In a single laboratory, Environmental Science and Engineering, using spiked wastewater samples, the average recoveries presented in Table 1 were obtained. The percent standard deviation of the recovery is also included in Table 1.[1] All recoveries are based on calibrations using the specific dithiocarbamate instead of ziram.

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TABLE 1

METHOD PERFORMANCE

Parameter	Method Detection Limit (µg/L)	Sample Type*	Number of Replicates	Spike (µg/L)	Mean Recovery (%)	Standard Deviation (%)
Maneb	15.3	1	7	31.5	97.1	15.5
Metham	3.7	2	7	20.1	94.5	5.9
		3	7	250	65.2	2.8
Ziram	1.9	4	8	32.2	100	2.0
		5	8	1050	96.2	10.0

*Sample type:
1 = Municipal wastewater.
2 = Mixture of 13% industrial (pesticide manufacturing) wastewater and 87% municipal wastewater.
3 = Industrial wastewater, pesticide manufacturing.
4 = Mixture of 40% industrial and 60% municipal wastewater.
5 = 7% industrial process water, 7% industrial wastewater, 86% municipal wastewater.

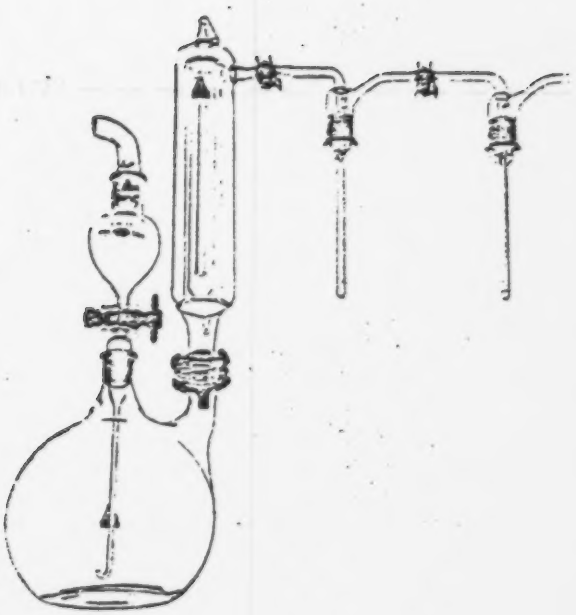

Figure 1. Dithiocarbamate hydrolysis apparatus.